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(57) Abstract

Machine dishwashing powder compositions are disclosed comprising a layered clay in the form of granulated particles obtained by: 1) co-granulating a finely divided clay with a solid particulate material using a water-soluble polymeric material as binding agent; 2) conglutinating a finely divided clay with sodium disilicate carrier material employing water-soluble nonionic surfactant as conglutinating agent; or 3) granulating a finely divided clay with water or an alkaline silicate solution. The granulated clay particles disperse well and do not cause clay deposit on and blocking of the dishwashing machine filter.

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MACHINE DISHWASHING COMPOSITION

This invention relates to machine dish- and warewashing compositions. These compositions are used for the cleaning of housewares such as pots, pans, dishes, cups, saucers, bottles, glassware, crockery, cutlery and other kitchen utensils in automatic-dishwashing and warewashing machines. For brevity sake these compositions are referred to in the description as machine dishwashing compositions.

Machine dishwashing compositions usually contain as main components a builder or builder mixture, buffering and/or alkaline agents, a bleaching agent which may be a chlorine or oxygen bleach, and lately also enzymes. Such machine dishwashing compositions are used in the main wash step of machine dishwashing and in general have a satisfactory cleaning performance.

It is, however, well known in the dishwashing art that the visual appearance of the cleaned article is a critical factor for a dishwashing composition to be satisfactory to the customer. Frequently after cleaning of an article a film is formed thereon, which results in the article showing a dull surface when dry, or spots are formed on an article upon drying, both phenomena causing the article to have an "unclean" visual appearance.

It is known from EP-A-0,139,329, EP-A-0,139,331 and EP-A-0,140,435 that the incorporation of an effective level of a layered clay in machine dishwashing compositions significantly reduces the problem of film and spot formation on the washed articles, thereby improving the so-called "glass appearance". Without wishing to be bound by any theory it is believed that the layered clay performs this task by providing a very large surface area in solution which then picks up food fragments that would otherwise re-deposit onto washed articles.

The layered clay minerals suitable for the above purpose of use belong to the geological classes of the smectites, the kaolins, the illites, the chlorites, the attapulgites and the mixed layer clays. Typical examples of specific clays belonging to these classes are:

smectites, e.g. montmorillonite, bentonite,pyrophylite, hectorite, saponite, sauconite, nontronite, talc, beidellite, volchonskoite, vermiculite;
kaolins, e.g. kaolinite, dickite, nacrite, antigorite, anauxite, halloysite, indellite, chrysotile;
illites, e.g. bravaisite, muscovite, paragonite, phlogopite, biotite;
chlorites, e.g. corrensite, penninite, donbassite, sudoite, pennine, clinochlore;
attapulgites, e.g. sepiolite, polygorskyte;
mixed layer clays, e.g. allevardite, vermiculite-biotite.

The layered clay minerals may be either naturally occurring or synthetic. Preferred clay minerals are natural or synthetic hectorites, montmorillonites and bentonites, and of these the hectorites are especially preferred. Many of the above clays are commercially available, and typical examples of commercial hectorites are the Laponites® ex Laporte Industries Ltd, England; Veegum Pro® and Veegum®F ex R.T. Vanderbilt, U.S.A.; the Barasyms®, Macaloids® and Propaloids®ex Baroid Division, National Read Comp. U.S.A.

Particularly preferred clays are the commercial synthetic hectorites ex Laporte Industries Ltd, known under the tradename Laponites such as Laponite S, Laponite XLS, Laponite RD, Laponite RDS and Laponite XLG.

The effective level of the layered clay to be included in machine dishwashing compositions generally lies within a range of 0.1 to 40%, preferably from 0.5 to 10%, and most

preferably from 0.5 - 5% by weight.

The present invention therefore relates to machine dishwasing compositions comprising a layered clay for reducing film and spot formation on the washed articles.

Although the glass appearance benefits of layered clay are real and can be truly demonstrated, there is a problem with the commercial grades of layered clay as supplied by manufacturers for use in "powdered" machine dishwashing composition.

Machine dishwashing powder compositions are not true fine powders, but consist of granules and particles of a size lying within the range of 0.2 to 2.0 mm, normally, from 0.25 to 1.5 mm. Finely divided clay powder as normally supplied cannot be used for incorporating in such granulated machine dishwashing compositions as it will segregate in the pack, with the consequence of non-uniformity of product composition in the pack upon reaching the consumer.

Commercial granule grades e.g. Laponite XLG (= standard grade) and Laponite XLS (= special grade) having mean particle size of about 0.6 mm as supplied by clay manufacturers can be used to largely overcome the segregation problem, but inherently appears to bring in another serious problem.

Repeated washing experiments in automatic dishwashing machines have revealed that a machine dishwashing product containing Laponite XLG and Laponite XLS granules can cause rapid blocking of the micro-filters of the dishwasing machines. This has subsequently been found to be Laponite clay which has gelled, but then not dispersed further and has become stuck to the filter.
The deposit on the filter built up rapidly and other materials (e.g. product and food residues) got stuck in the

gel accelerating the rate of blockage. The rate at which build-up occurred depends upon the water-hardness. It has been found that clay build-up was faster in harder water, probably due to higher ionic strength retarding dispersion. This phenomenon is not only a nuisance from an operational point of view but is also a problem for both performance and cost reasons, because if the clay is stuck in the filter, it will not be available in the wash solution and thus is not giving a maximum glass appearance benefit, which means that an expenditure for an expensive ingredient in terms of money is literally going down the drain.

Accordingly it is an object of the present invention to provide means for incorporating clay in machine dishwashing powder compositions without the problem of segregation in the pack and without the problem of clay deposit on the micro-filters.

It is another object of the invention to provide a machine dishwasing powder composition comprising a clay material which does not segregate in the pack and does not deposit on and blocking the dishwashing machine filter.

It has now surprisingly been found that these and other objects which will be apparent in the further description of the invention can be achieved if the clay material is provided in the form of granules of a size of about 0.2 - 2.0 mm, obtained by:

1) co-granulating a finely divided layered clay material with a solid particulate material using a water soluble film-forming polymeric material of average molecular weight of from about 500-1.000.000, as binding agent;
2) conglutinating a finely divided layered clay material with sodium disilicate carrier material employing a water-soluble nonionic surface active agent as the conglutinating agent; or

3) granulating a finely divided layered clay material with water or an alkaline silicate solution.

Accordingly the invention provides a machine dishwashing powder composition comprising a layered clay, characterized in that said layered clay is in the form of granulated particles of a size of from about 0.2-2.0 mm, obtained by:

1) co-granulating a finely divided layered clay material with a solid particulate material using a water soluble film-forming polymeric material of average molecular weight of from about 500-1.000.000, as binding agent;
2) conglutinating a finely divided layered clay material with sodium disilicate carrier material employing a water-soluble nonionic surface active agent as the conglutinating agent; or
3) granulating a finely divided layered clay material with water or an alkaline silicate solution.

Thus the granulated clay usable in the present invention may be:

1) a co-granulate comprising a matrix of a finely divided layered clay material, a solid particulate material and a water-soluble film-forming polymeric binder material having average molecular weight of from about 500-1,000,000;
2) a conglutinate comprising a core of sodium disilicate carrier material, a coating layer of a nonionic surface-active agent enrobing said core, and a finely divided layered clay material attached to the glutinous coating layer of the core, or
3) an agglomerate of finely divided layered clay material with water or an alkaline silicate solution as binder.

Preferred granulated clay is a co-granulate as defined and obtained under 1) hereinbefore. Suitable solid particulate

materials for use herein are for example carbonates, citrates, silicates, peroxygen bleaching agents, bleach activators, bleach catalysts and mixtures thereof. Crystalline materials which by themselves are ingredients of machine dishwashing compositions are preferred.

Typically granulated clay particles obtained by co-granulation will have a composition comprising:

(i) from 20 - 70%, preferably from 25-40% by weight of a finely divided layered clay material;

(ii) from 25 - 70%, preferably from 50-65% by weight of solid particulate material selected from the group of carbonates, citrates, silicates, peroxygen, bleaching agents, bleach activators and bleach catalysts, and mixtures thereof; and

(iii) from 2 - 10%, preferably from 5-8.5% by weight of a water-soluble film-forming polymeric material having average molecular weight of from about 500 - 1.000.000; and

(iv) from 0 - 10%, preferably from 2.5-10% by weight of water

A preferred solid particulate material to co-granulate with is a bleach activator, especially N, N, N^1, N^1-tetraacetyl ethylene diamine (TAED).

If a bleach catalyst is also used this can also be incorporated in the granule composition. It is furthermore preferred that the granule composition is exempt of inert non-functional ingredients, i.e. fillers, such as sodium sulphate.

The preferred clays for use in the present invention are the commercially available synthetic hectorite in finely divided powdered form ex Laporte Industries Ltd, known as Laponite® clay.

Film forming polymeric materials which can be used in the invention are, for example, carbohydrates and derivatives, such as carbohydrate ethers; polymers or copolymers from vinyl monomers, such as vinylacetate (and its hydrolysate vinyl alcohol), vinyl pyrrolidone, methyl acrylate, acrylic acid, methacrylic acid, maleic acid (anhydride), styrene, styrene sulphonate or mixtures thereof. Specific examples of suitable polymeric materials are polyvinyl acetate, polyvinyl pyryolidone, copolymers of polyvinyl alcohol/polyvinyl acetate; carboxy methyl cellulose; dextrine modified vinylacetate polymers; and homo- or copolymeric polycarboxylic acids or salts thereof, such as the polyacrylic acids or polyacrylates, copolymers of maleic acid (anhydride) and acrylic or methacrylic acid, and copolymers of maleic acid (anhydride) and vinyl-methyl ether. Preferred materials are the copolymers of maleic acid (anhydride) and (meth)acrylic acid , such as being sold under the trade names Sokalan® CP4 and Sokalan® CP5 ex BASF.

The nonionic surface-active agent for use as coating layer to render the surfaces of the core material glutinous can be any nonionic surfactant which is liquid or semi-paste-like at room temperature. Higher melting liquifiable nonionic surface-active agents may also be used. Examples of suitable nonionic surface active agents are C_8-C_{20} monohydric aliphatic alcohols condensed with 5 to 25 moles of ethylene oxide, such as tallow fatty alcohol condensed with 20-25 moles of ethylene oxide, isotridecyl alcohol condensed with 7-11 ethylene oxide, secondary C_{11}-C_{15} alcohols condensed with 3-10 ethylene oxide, fatty acid mono- and di-alkylolamides with 10-20 carbonatoms in the fatty acid residue and ethoxylated derivatives thereof. Preferred nonionic surfactants are however the low to non-foaming nonionic surfactants, normally incorporated in machine dishwashing compositions to improve detergency and to suppress excessive foaming due to some protein soil.

Examples thereof are the low-to-non-foaming ethoxylated straight chain alcohols of the Plurafac® RA series, supplied by the Eurane Company; of the Lutensol® LF series, supplied by the BASF Company; of the Triton® DF series, supplied by the Rohm & Haas Company; and of the Synperonic® LF series, supplied by the ICI Company.

The granulated clay particles can be manufactured by using any known granulation technique e.g. with a pan granulator, a rotating drum or a Schugi® granulator, such as the Schugi Flexomix® 160, wherein 1) an agitated powder mixture comprising the clay is sprayed with the proper amount of polymer-solution, optionally followed by drying e.g. in a fluid bed drier; 2) a nonionic surface active agent is mixed with a granular sodium disilicate carrier material and subsequently affixing the finely divided clay thereon; or 3) an agitated clay powder is sprayed with water or an alkaline silicate solution.

The granulated clay particles disperse well and do not cause deposits of clay material on or blocking of the micro-filter of dishwashing machines, provided the clay material used in the granulation process is a powder of a size that is smaller than the micro-filter mesh size. Finely divided clay powder as supplied by manufacturers have particle size of about 20 to 200 μm, which is normally suitable for use in the present invention.

The machine dishwashing powder of the invention will normally also contain a builder or builder mixture, buffering and/or alkaline agents, and a bleaching agent, and optionally but preferably also an enzyme or mixtures of enzymes.

<u>The builder material</u>

Builder materials (phosphates and non-phosphate builder materials) are well-known in the art and many types of

organic and inorganic compounds have been described in literature. They are normally used in all sorts of cleaning compositions to provide alkalinity and buffering capacity, prevent flocculation, maintain ionic strength, extract metals from soils and/or remove alkaline-earth metal ions from washing solutions.

The builder material usable herein can be any one or mixture of the various phosphate and preferably non-phosphate builder materials, such as for example the alkalimetal citrates, carbonates and bicarbonates; nitrilotriacetic acid (NTA); dipicolinic acid (DPA); oxydisuccinic acid (ODS); alkenylsuccinates (AKS); and zeolites. They may be present in the composition of the invention in an amount of from 10% up to about 90% by weight, preferably from 20% to 80% by weight.

Particularly preferred builders are citrates, alkenylsuccinates, carbonates, bicarbonates, zeolites, and mixtures thereof.

The buffering and/or alkaline agent

This is normally an alkalimetal silicate, preferably sodium silicate at a level of from about 1 to about 70% by weight, preferably from 5 to 40% by weight. This material is employed as a cleaning ingredient, source of alkalinity, metal corrosion inhibitor and protector of glaze on china tableware. Especially effective is sodium silicate having a mol ratio of SiO_2:Na_2O of from about 1.0 to about 3.3., preferably from about 1.8 to about 2.5, normally referred to as sodium disilicate.

The bleaching agent

The amount of bleaching agent will preferably lie in a range from 1 to 30% by weight. Alkali metal hypochlorite may be incorporated in liquid compositions. Other chlorine bleaches

which may be incorporated are alkali metal salts of di- and tri-chloro and di- and tri-bromo cyanuric acids.

Preferred bleaches are the peroxygen bleaches, such as sodium perborate (tetra- or monohydrate) or sodium percarbonate. These are preferably used in conjunction with a bleach activator which allows the liberation of active oxygen species at a lower temperature. Numerous examples of activators of this type, often also referred to as bleach or peracid precursors, are known in the art. Preferred bleach activators are tetraacetyl ethylene diamine (TAED), glucose pentaacetate (GPA) and the mono-long chain acyl tetraacetyl glucoses as disclosed in WO 91/10719, but other activators such as choline sulphophenylcarbonate (CSPC) as disclosed in US Patents 4,751,015 and 4,818,426 can be used. The amounts of sodium perborate or percarbonate and bleach activator in the compositions preferably do not exceed 20% and 10% by weight respectively, e.g. from 4-20% and from 2-10% by weight respectively.

Another peroxygen bleach is potassium monopersulphate. Further peroxygen bleaches which may be used are the solid organic peroxyacids and their metal salts. Typical peroxy-acids include:

(i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy-α-naphthoic acid;

(ii) aliphatic and substituted aliphatic monoperoxy acids, e.g. peroxylauric acid and peroxystearic acid;

(iii) 1, 12-diperoxydodecanedioic acid (DPDA);

(iv) 1, 9-diperoxyazelaic acid;

(v) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;

(vi) 2-decyldiperoxybutane-1,4-dioic acid; and

(vii) phthaloylamido peroxycaproic acid (PAP)

Instead of or together with said bleach activators, a bleach catalyst, such as the manganese complexes of EP-A-458,397

and the sulphonimines of US Patents 5,041,232 and 5,047,163 may also be added.

Enzymes

Amylolytic and proteolytic enzymes are normally used. The amylolytic enzymes usable herein can be those derived from bacteria or fungi. Preferred amylolytic enzymes are those prepared and described in GB Patent No. 1,296,839, cultivated from the strains of Bacillus licheniformis NCIB 8061, NCIB 8059, ATCC 6334, ATCC 6598, ATCC 11945, ATCC 8480 and ATCC 9945 A. Examples of such amylolytic enzymes are those produced and distributed under the Trade-names of SP-95® and Termamyl® by Novo Industri A/S, Copenhagen, Denmark. These amylolytic enzymes are generally presented as granules and may have enzyme activities of from about 2 to 10 Maltose units/milligram. They may be present in the composition of the invention in amounts such that the final composition has amylolytic enzyme activity of from 10^3 to 10^6 Maltose Units/Kilogram.

The amylolytic activity as referred to herein can be determined by the method as described by P. Bernfeld in "Method of Enzymology" Volume I (1955) page 149.

The proteolytic enzymes usable herein are for example the subtilisins which are obtained from particular strains of B. Subtilis and B. licheniformis, such as the commercially available substilisins Maxatase® supplied by Gist-Brocades NV, Delft, Holland, and Alcalase®, supplied by NOVO Industri A/S Copenhagen, Denmark. Particularly suitable are proteases obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available from NOVO Industri A/S under the Trade names of Esperase® and Savinase®. The preparation of these and analogues enzymes is described in GB Patent No. 1,243,784. These enzymes are generally presented as granules, e.g. marumes, prills, T-granulates etc., and may have enzyme

activities of from 500 to 1700 Glycine Units/mg. The proteolytic enzyme activity can be determined by the method as described by M.L. Anson in "Journal of General Physiology" Vol. 22 (1938), page 79 (one Anson unit/gram = 733 Glycine Units/milligram).

In the compositions of the invention proteolytic enzymes may be present in amounts such that the final composition has proteolytic enzyme activity of from about 10^6 to 10^8 Glycine Units/Kilogram.

Other enzymes, such as lipolytic enzymes may also be incorporated to improve fat removal. Typical examples of commercial lipolytic enzymes are Lipase YL, Amano CE, Wallerstein AW, Lipase My, and Lipolase ex Novo Ind.

Other optional ingredients

Surfactants though not strictly essential may also be present for detergency, soil removal, foam depression and/or as rinse aids. If present they can be used in an amount of up to about 60% by weight depending upon their type and properties. Normally in a properly built or highly built composition as is conventional, only small amounts of low- to non-foaming nonionic surfactant in the order of 0.1-5% by weight are preferably used, to aid detergency and particularly to suppress excessive foaming caused by some protein soil. Higher amounts i.e. 5-60% by weight of highly detersive surfactants, such as the high HLB nonionic surfactants, the anionic sulphate or sulphonate surfactants and the alkyl polyglycoside class of surfactants, may be used in normally lower builder containing active-based compositions.

Zinc salts, both soluble and insoluble zinc salts, can also be incorporated as adjuncts for minimizing glass corrosion.

An inert particulate filler especially sodium sulphate may

also be incorporated, though in compact powdered composition it should desirably be omitted as practically possible.

The presence of alkali-metal or alkaline earth metal salts of amino polyphosphonic acids such as the sodium or calcium salt of ethylene diamine tetra methylene phosphonic acid, and ethylene hydroxy dimethylene phosphonate may also be preferred because of their stabilizing effect on percompound bleaches and/or their anti-scaling properties. Also polycarboxylate polymeric substances, such as the maleic acid/methacrylic acid copolymers, known under the Trade Name Sokalan CP5® may be present to aid in the inhibition of scaling.

The products of the present invention are preferably formulated such that they provide a wash liquor with a pH of between 9 and 11, more preferably from 9.5-10.5 (at a concentration of 0.3% by weight in water).

The invention will now be illustrated by way of the following examples (percentages are by weight unless otherwise stated).

Examples I-II

A 2:1 w/w TAED/Laponite powder mix was dosed to a Schugi Flexomix 160 equipment (3000 rpm; blades at +2 degrees) at 420 kg/hr. In one experiment a 30% Sokalan CP5 solution was used as liquid binder and in another experiment a 34% Sokalan CP5 solution was used. The liquid binder was dosed at a gradually increasing flow rate, until (after approx. 2 minutes) the granulates looked good. Then the liquid feed was kept constant and the wet granulate was charged to the fluid bed drier. At a reasonable fill of the fluid bed (approx. 30 kg) the granulation was stopped and drying continued until the bed temperature was 50°C. Each experiment was dried at two water contents of 5% and 10% by

weight.

The following granules were obtained:

Compositions	I (% by weight)		II (% by weight)	
TAED	58.6	55.6	57.7	54.7
Laponite	29.4	27.8	28.9	27.4
CP5	7.0	6.6	8.4	7.9
Water	5	10	5	10
BD	540 g/l		542 g/l	
Particle size:	5% > 1.4 mm		7% > 1.4 mm	
	7.5% < 0.25 mm		7.5% < 0.25 mm	

Examples III-IV

Repeat Washing experiments were carried out in a Miele dishwashing machine using water of 17°FH in a clean system with machine dishwashing compositions of the following formulations:

	% by weight		
	III	IV	A
Sodium citrate	40	36.5	40.7
Sodium disilicate	34	34	34
Na-perborate monohydrate	8	8	8
Enzyme (protease + amylase)	4	4	4
Nonionic surfactant	2	2	2
Sokalan CP5	6	6	6
TAED	*{ 3.5	3.5	3.5
Laponite clay	{ 1.8	1.8 }*	1.8**
Sokalan CP5	{ 0.4	0.4 }	--
Water	{ 0.3	0.3 }	--
Sodium carbonate	--	3.5 }	--

* granulated clay according to the invention

** 1) Laponite XLG - standard granules ex Laporte Industries

2) Laponite XLS - special granules containing pyrophosphate as dispersion aid ex Laporte Industries

The appearance of the filter and weight of residue on the filter were determined after 20 repeat washes.

The following results were obtained:

Composition	Laponite clay residue in Miele Filter After 20 repeat washes
III	0,00 g
IV	0,00 g
$A_{(1)}$	0,15 g
$A_{(2)}$	0,05 g

The above data show that the use of finely divided Laponite clay granulated according to the invention did not cause filter blocking at all. The filter remained clean after 20 repeat washes. The data also show that the commercial Laponite® granules gave clay build-up on the filters. The presence of a dispersion aid added in the Laponite granule (Laponite XLS in Composition $A_{(2)}$) could reduce, but did not prevent residue build-up on the filter.

Example V-VII

The same base formulation of Examples III-IV (formulation A without clay) was used, wherein part (10%) of the disilicate and part of the nonionic surfactant (1%) were taken out for preparing conglutinated Laponite clay granules (V).

In another experiment the same base formulation was used wherein the Laponite clay was incorporated as granulates with water (VI) and granulates with alkaline silicate solution (VII).

The appearance of the filter and weight of residue on the filter were determined after 20 repeat washes under the same

conditions as used in Examples III-IV.

The following results were obtained:

Composition	Laponite clay residue in Miele filter after 20 repeat washes
V	0.00 g.
VI	0.01 g.
VII	0.01 g.

The above data again show that the use of finely divided Laponite clay granulated according to the invention gave no or substantially no clay build-up on the filter.

CLAIMS

1. A machine dishwashing powder composition comprising a layered clay, characterised in that the clay material is in the form of granules of a size of about 0.2-2.0 mm. obtained by:
   1) co-granulating a finely divided layered clay material with a solid particulate material using a water-soluble film-forming polymeric material of average molecular weight of from about 500 to 1.000.000, as binding agent;
   2) conglutinating a finely divided layered clay material with sodium disilicate carrier material employing a water-soluble nonionic surface active agent as the conglutinating agent; or
   3) granulating a finely divided layered clay material with water or an alkaline silicate solution.

2. A composition according to claim 1, characterized in that the clay granules are co-granulates as obtained by process 1).

3. A composition according to claim 1 or 2, characterized in that said solid particulate material is selected from the group of carbonates, citrates, silicates, peroxygen bleaching agents, bleach activators, bleach catalysts, and mixtures thereof.

4. A composition according to claim 3, characterized in that said solid particulate material comprises a bleach activator.

5. A composition according to claim 4, characterized in that said bleach activator is N, N, N^1, N^1-tetraacetylethylene diamine.

6. A composition according to any of the preceding claims

2-5, characterized in that said co-granulate comprises:

(i) from 20-70% by weight of a finely divided layered clay material;

(ii) from 25-70% by weight of said solid particulate material;

(iii) from 2-10% by weight said water-soluble polymeric material; and

(iv) from 0-10% by weight of water.

7. A composition according to claim 6, characterized in that said co-granulate comprises:

(i) from 25-40% by weight of said clay material;

(ii) from 50-65% by weight of said solid particulate material;

(iii) from 5-8.5% by weight of said water-soluble polymeric material; and

(iv) from 2.5-10% by weight of water.

8. A composition according to any of the preceding claims 1-7, characterized in that said layered clay is a synthetic hectorite.

9. A composition according to any of the preceding claims 1-8, characterized in that the granulated clay particles are free of sodium sulphate.

10. A composition according to any of the preceding claims 1-9, characterized in that the water-soluble polymeric material is a copolymer of maleic acid(anhydride) and (meth) acrylic acid.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 93/01461

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C11D3/12

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C11D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	EP,A,0 419 970 (HENKEL KGAA.) 3 April 1991 see the whole document	1-3,8,10
X	EP,A,0 240 057 (UNILEVER) 7 October 1987 see the whole document	1-5,8,10
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° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
25 OCTOBER 1993	02.11.93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	SERBETSOGLOU A.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

EP 9301461
SA 75042

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 25/10/93
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